

The present invention relates to a polyethylene moulding compound having a multi-modal molecular weight distribution and to a method for the production of this moulding compound in the presence of a catalytic system comprising a Ziegler catalyst and co-catalyst via a multistep reaction sequence consisting of successive liquid-phase polymerizations, and to hollow articles produced from the moulding compound by extrusion blow moulding.

Polyethylene is widely used for the production of mouldings and containers since it is a material having a low inherent weight which nevertheless has particularly high mechanical strength, high corrosion resistance to moisture and water in combination with atmospheric oxygen and absolutely reliable long-term resistance and since polyethylene has good chemical resistance and in particular can easily be processed for bottles, canisters and fuel tanks in motor vehicles.

A raw material having an even broader molecular weight distribution is described in US Patent 5,338,589 and is prepared using a highly active catalyst disclosed in WO 91/18934 in which magnesium alkoxide is employed in the form of a gelatinous suspension. Surprisingly, it has been found that the use of this material in mouldings, in particular in pipes, facilitates a simultaneous improvement in the properties of stiffness and creep tendency, which are usually contradictory in partially crystalline thermoplastics, on the one hand, and stress cracking resistance and toughness on the other hand.

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The known bimodal products are distinguished, in particular, by good processing properties at the same time as an outstanding stress cracking/stiffness ratio. This combination of properties is of particular importance in the production of hollow articles from plastics, such as bottles, canisters and fuel tanks in motor vehicles. In addition to this property combination, however, the production of plastic hollow articles requires the highest possible swelling rate of the plastic melt, since the swelling rate is directly responsible for enabling the optimum setting of wall thickness control, the formation of the weld line and the weldability in industrial production in extrusion blow moulding.

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It is known that plastics having high swelling rates can be produced well using so-called Phillips catalysts, i.e. polymerization catalysts based on chromium compounds. However, the plastics produced in this way have an unfavourable stress cracking/stiffness ratio compared with the known plastics having a bimodal molecular weight distribution.

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EP-A-0 797 599 discloses a process which even gives a polyethylene having a trimodal molecular weight distribution in successive gas-phase and liquid-phase polymerizations. Although this polyethylene is already very highly suitable for the production of hollow articles in extrusion blow moulding plants, it is, however, still in need of further improvement in its processing behaviour owing to the plastic melt swelling rate, which is still too low.

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The object of the present invention was the development of a polyethylene moulding compound by means of which an even better ratio of stiffness to stress cracking resistance compared with all known materials can be achieved and which, in addition, has a high swelling rate of its melt, which, in the production of hollow articles by the extrusion blow moulding process, not only enables optimum wall thickness control, but at the same time also facilitates excellent weld line formation and wall thickness distribution.

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- This object is achieved by a moulding compound of the generic type mentioned at the outset, whose characterizing features are to be regarded as being that it comprises from 30 to 60% by weight of a low-molecular-weight ethylene homopolymer A, from 65 to 30% by weight of a high-molecular-weight copolymer B comprising ethylene and another olefin having from 4 to 10 carbon atoms, and from 1 to 30% by weight of an ultrahigh-molecular-weight ethylene homopolymer or copolymer C, where all percentages are based on the total weight of the moulding compound.
- 10 The invention furthermore also relates to a method for the production of this moulding compound in cascaded suspension polymerization, and to hollow articles made from this moulding compound with very excellent mechanical strength properties.
- 15 The polyethylene moulding compound according to the invention has a density in the range $\geq 0.940 \text{ g/cm}^3$ at a temperature of 23°C and has a broad trimodal molecular weight distribution. The high-molecular-weight copolymer B comprises small proportions of up to 5% by weight of further olefin monomer units having from 4 to 10 carbon atoms. Examples of comonomers of this type are 1-butene, 1-pentene, 20 1-hexene, 1-octene or 4-methyl-1-pentene. The ultrahigh-molecular-weight ethylene homopolymer or copolymer C may optionally also comprise an amount of from 0 to 10% by weight of one or more of the above-mentioned comonomers.

The moulding compound according to the invention furthermore has a melt flow index, in accordance with ISO 1133, expressed as $\text{MFI}_{190/5}$, in the range from 0.01 to 10 dg/min and a viscosity number VN_{tot} , measured in accordance with ISO/R 1191 in decalin at a temperature of 135°C , in the range from 190 to $700 \text{ cm}^3/\text{g}$, preferably from 250 to $500 \text{ cm}^3/\text{g}$.

- 30 The trimodality can be described as a measure of the position of the centres of the

three individual molecular weight distributions with the aid of the viscosity numbers VN in accordance with ISO/R 1191 of the polymers formed in the successive polymerization steps. The following band widths of the polymers formed in the individual reaction steps should be taken into account here:

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The viscosity number VN_1 measured on the polymer after the first polymerization step is identical with the viscosity number VN_A of the low-molecular-weight polyethylene A and is in accordance with the invention in the range from 40 to $180 \text{ cm}^3/\text{g}$.

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VN_B of the relatively high-molecular-weight polyethylene B formed in the second polymerization step can be calculated from the following mathematical formula:

$$VN_B = \frac{VN_2 - w_1 \cdot VN_1}{1 - w_1}$$

15 where w_1 represents the proportion by weight of the low-molecular-weight polyethylene formed in the first step, measured in % by weight, based on the total weight of the polyethylene having a bimodal molecular weight distribution formed in the first two steps, and VN_2 represents the viscosity number measured on the polymer after the second polymerization step. The value calculated for VN_B is normally in the
20 range from 150 to $800 \text{ cm}^3/\text{g}$.

VN_C for the ultrahigh-molecular-weight homopolymer or copolymer C formed in the third polymerization step is calculated from the following mathematical formula:

$$VN_C = \frac{VN_3 - w_2 \cdot VN_2}{1 - w_2}$$

25 where w_2 represents the proportion by weight of the polyethylene having a bimodal molecular weight distribution formed in the first two steps, measured in % by weight,

based on the total weight of the polyethylene having a trimodal molecular weight distribution formed in all three steps, and VN_3 represents the viscosity number which is measured on the polymer after the third polymerization step and is identical with the VN_{tot} already mentioned above. The value calculated for VN_c is in accordance
5 with the invention in the range from 900 to 3000 cm^3/g .

The polyethylene is obtained by polymerization of the monomers in suspension or at temperatures in the range from 20 to 120°C, a pressure in the range from 2 to 60 bar and in the presence of a highly active Ziegler catalyst composed of a transition-metal
10 compound and an organoaluminium compound. The polymerization is carried out in three steps, i.e. in three successive steps, with the molecular weight in each case being regulated with the aid of metered-in hydrogen.

The polymerization catalyst's long-term activity, which is necessary for the cascaded
15 procedure described above, is ensured by a specially developed Ziegler catalyst. A measure of the suitability of this catalyst is its extremely high hydrogen responsiveness and its high activity, which remains constant over a long period of from 1 to 8 hours. Specific examples of a catalyst which is suitable in this manner are the products cited in EP-A-0 532 551, EP-A-0 068 257 and EP-A-0 401 776 of the reaction
20 of magnesium alkoxides with transition-metal compounds of titanium, zirconium or vanadium and an organometallic compound of a metal from groups I, II or III of the Periodic Table of the Elements.

Besides the polyethylene, the polyethylene moulding compound according to the
25 invention may also comprise further additives. Additives of this type are, for example, heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, peroxide-destroying compounds, basic costabilizers in amounts of from 0 to 10% by weight, preferably from 0 to 5% by weight, but also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, anti-
30 statics, blowing agents or combinations thereof in total amounts of from 0 to 50% by

weight, based on the total weight of the mixture.

The moulding compound according to the invention is particularly suitable for the production of hollow articles, such as fuel canisters, chemical-resistant containers, canisters, drums and bottles, by firstly plasticating the polyethylene moulding compound in an extruder at temperatures in the range from 200 to 250°C, and then extruding the compound through a die into a blow mould, and cooling it therein.

For conversion into hollow articles, use can be made of both conventional single-screw extruders having a smooth feed zone and high-performance extruders having a finely grooved barrel and forced conveying feed section. The screws are typically designed as decompression screws with a length of from 25 to 30 D (D = diameter). The decompression screws have a discharge zone in which temperature differences in the melt are compensated and in which the relaxation stresses formed due to shearing are intended to be dissipated.

Example 1 (according to the invention):

The polymerization of ethylene was carried out in a continuous method in three reactors connected in series. A Ziegler catalyst, a sufficient amount of suspension medium, ethylene and hydrogen were fed into the first reactor. The amount of ethylene and hydrogen was set in such a way that one part by volume of hydrogen was present per nine parts by volume of ethylene.

The catalyst was a Ziegler catalyst as described in Example 2 of WO 91/18934, which had the catalyst component a having the operation number 2.2 therein, and which is added together with a co-catalyst comprising an organometallic compound of a metal from group I, II or III of the Periodic Table of the Elements.

The catalyst was metered continuously into the first reactor with the co-catalyst and

triethylamine in the ratio 1:10 (mol/mol).

5 The polymerization in the first reactor was carried out at a temperature of 76°C and a pressure of 0.78 MPa for a period of 3.3 hours with a hydrogen content in the gas space of from 67 to 68% by volume.

The suspension from the first reactor was then transferred into a second reactor, in which the amount of hydrogen had been reduced to 5 parts by volume in the gas space and the amount of C₄ comonomer had been increased to 5 parts by volume.
10 The reduction in the amount of hydrogen was carried out via interim H₂ decompression.

The polymerization in the second reactor was carried out at a temperature of 84°C and a pressure of 0.5 MPa for a period of 54 minutes.

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The suspension from the second reactor was transferred into the third reactor via further interim H₂ decompression, by means of which the amount of hydrogen in the gas space of the third reactor is set to $\leq 5\%$ by volume.

The polymerization in the third reactor was carried out at a temperature of 47°C and
20 a pressure of ≤ 0.23 MPa for a period of 30 minutes.

The polymer suspension leaving the third reactor was fed to granulation after removal of the suspension medium and drying.

25 The viscosity numbers and proportions w_A , w_B and w_C of polymer A, B and C applying to the polyethylene moulding compound produced in accordance with Example 1 are given in Table 1 shown below together with the corresponding data for the moulding compounds produced in accordance with the following Examples 2 to 4.

Example 2 (according to the invention)

Example 1 was repeated with the following changes:

5 The polymerization in the first reactor was carried out at a temperature of 82°C and a pressure of 0.89 MPa for a period of 2.6 hours with a hydrogen content of 68% by volume in the gas space of the reactor.

10 The suspension from the first reactor was then transferred into a second reactor, in which the amount of hydrogen had been reduced to 10 parts by volume in the gas space of the reactor and the amount of C₄ comonomer had been increased to 0.7 parts by volume in the gas space of the reactor. The reduction in the amount of hydrogen was again carried out via interim H₂ decompression.

15 The polymerization in the second reactor was carried out at a temperature of 80°C and a pressure of 0.37 MPa for a period of 66 minutes.

20 The suspension from the second reactor was transferred into the third reactor, and the amount of hydrogen in the gas space of the third reactor was set to 0.6% by volume and that of C₄ comonomer to 0.8% by volume.

The polymerization in the third reactor was carried out at a temperature of 80°C and a pressure of 0.15 MPa for a period of 36 minutes.

25 The viscosity numbers and proportions w_A, w_B and w_C of polymer A, B and C applying to the polyethylene moulding compound produced in accordance with Example 2 are given in Table 1 shown below together with the corresponding data for the moulding compounds produced in accordance with the other examples.

Example 3 (according to the invention)

Example 2 was repeated with the following changes:

5 The polymerization in the first reactor was carried out at a temperature of 80°C and a pressure of 0.74 MPa for a period of 2.1 hours with a hydrogen content of 65% by volume in the gas space of the reactor.

10 The suspension from the first reactor was then transferred into a second reactor, in which the amount of hydrogen had been reduced to 4.1 parts by volume in the gas space of the reactor and the amount of C₄ comonomer had been increased to 1.1 parts by volume in the gas space of the reactor. The reduction in the amount of hydrogen was again carried out via interim H₂ decompression.

15 The polymerization in the second reactor was carried out at a temperature of 80°C and a pressure of 0.24 MPa for a period of 54 minutes.

The suspension from the second reactor was transferred into the third reactor, and the amount of hydrogen in the gas space of the third reactor was set to 1.1% by volume and that of C₄ comonomer to 0.8% by volume.

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The polymerization in the third reactor was carried out at a temperature of 60°C and a pressure of 0.12 MPa for a period of 30 minutes.

25 The viscosity numbers and proportions w_A , w_B and w_C of polymer A, B and C applying to the polyethylene moulding compound produced in accordance with Example 3 are given in Table 1 shown below together with the corresponding data for the moulding compounds produced in accordance with the other examples.

Example 4 (according to the invention)

Example 3 was repeated with the following changes:

5 The polymerization in the first reactor was carried out at a temperature of 80°C and a pressure of 0.82 MPa for a period of 2.2 hours with a hydrogen content of 74% by volume in the gas space of the reactor.

10 The suspension from the first reactor was then transferred into a second reactor, in which the amount of hydrogen had been reduced to 4.0 parts by volume in the gas space of the reactor and the amount of C₄ comonomer had been increased to 1.3 parts by volume in the gas space of the reactor. The reduction in the amount of hydrogen was again carried out via interim H₂ decompression.

15 The polymerization in the second reactor was carried out at a temperature of 80°C and a pressure of 0.20 MPa for a period of 54 minutes.

20 The suspension from the second reactor was transferred into the third reactor, and the amount of hydrogen in the gas space of the third reactor was set to 1.0% by volume and that of C₄ comonomer to 1.0% by volume.

The polymerization in the third reactor was carried out at a temperature of 60°C and a pressure of 0.08 MPa for a period of 30 minutes.

25 The viscosity numbers and proportions w_A, w_B and w_C of polymer A, B and C applying to the polyethylene moulding compound produced in accordance with Example 2 are given in Table 1 shown below together with the corresponding data for the moulding compounds produced in accordance with the other examples.

Comparative Example (CE):

Example 1 was repeated, but with the difference that the polymerization was terminated after the second reaction step.

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The polymerization in the first reactor was carried out at a temperature of 84°C and a pressure of 0.90 MPa for a period of 4.2 hours with a hydrogen content of 76% by volume in the gas space of the reactor.

- 10 The suspension from the first reactor was then transferred into a second reactor, in which the amount of hydrogen had been reduced to 3.0 parts by volume in the gas space of the reactor and the amount of C₄ comonomer had been increased to 1.9 parts by volume in the gas space of the reactor. The reduction in the amount of hydrogen was again carried out via interim H₂ decompression.

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The polymerization in the second reactor was carried out at a temperature of 83°C and a pressure of 0.21 MPa for a period of 80 minutes.

- 20 This gave a polyethylene having a bimodal molecular weight distribution, as corresponds to the prior art in accordance with EP-A 603 935.

Table 1

Example	1	2	3	4	CE
W _A	0.35	0.45	0.55	0.55	0.52
W _B	0.55	0.45	0.35	0.35	0.48
W _C	0.10	0.10	0.10	0.10	0
VN _i [cm ³ /g]	80	80	100	60	55
MFR(2)	3.5	2.3	2.3	2.0	0.7
MFR(3)	1.2	0.7	0.55	0.56	---
MFR/5 [g/10']	1.07	0.55	0.30	0.36	0.4
MFR/21.6 [g/10']	17.9	11	9.5	13.8	13.4
FRR 21.6/5	17	20	31.6	36.3	33.6
VN _{tot} [cm ³ /g]	306	325	392	373	329
Density [g/cm ³]	0.954	0.952	0.953	0.954	0.954
FT 0°C [kJ/m ²]	9.6	10.7	12.6	7.8	6
FCM [N/mm ²]	1270	1200	1240	1280	1275
SR rheometer [%]	200	151	153	143	91
SCR [h]	3.7	16	54.2	54.1	39

The abbreviations for the physical properties in Table 1 have the following meanings:

- FCM = flexural creep modulus, measured in accordance with ISO 54852-Z4 in N/mm^2 as the one-minute value,
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- SCR = stress cracking resistance of the moulding compound according to the invention. It is determined by an internal measurement method. This laboratory method has been described by M. Fleißner in *Kunststoffe 77* (1987), pp. 45 ff. This publication shows that there is a correlation between the determination of slow crack growth in the creep test on test bars with all-round
10 notches and the brittle branch in the long-term failure test under internal hydrostatic pressure in accordance with ISO 1167. A shortening of the time to failure is achieved by shortening the crack initiation time by the notches (1.6 mm/razor blade) in ethylene glycol as stress crack-promoting medium at
15 a temperature of 80°C and a tensile stress of 3.5 MPa. The samples are produced by sawing three test specimens measuring 10 x 10 x 90 mm out of a pressed sheet with a thickness of 10 mm. The test specimens are provided with all-round notches in the centre using a razor blade in a notching device produced especially for the purpose (shown in Figure 5 in the publication by
20 Fleißner). The notch depth is 1.6 mm.
- FT = fracture toughness of the moulding compound according to the invention. It is likewise determined by an internal measurement method on test bars measuring 10 x 10 x 80 mm which had been sawn out of a pressed
25 sheet with a thickness of 10 mm. Six of these test bars are notched in the centre using a razor blade in the notching device mentioned above. The notch depth is 1.6 mm. The measurement is carried out substantially in accordance with the Charpy measurement method in accordance with ISO 179 with modified test specimens and modified impact geometry (distance between supports). All test specimens are conditioned to the measurement temperature of
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0°C over a period of from 2 to 3 hours. A test specimen is then placed without delay onto the support of a pendulum impact tester in accordance with ISO 179. The distance between the supports is 60 mm. The drop of the 2 J hammer is triggered, with the drop angle being set to 160°, the pendulum length to 225 mm and the impact velocity to 2.93 m/sec. In order to evaluate the measurement, the quotient of the impact energy consumed and the initial cross-sectional area at the notch a_{FM} in mJ/mm^2 is calculated. Only values for complete fracture and hinge fracture can be used here as the basis for a common mean (see ISO 179).

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- SR = swelling rate, measured in a high-pressure capillary rheometer at a shear rate of 1440 1/s in a 2/2 round-hole die with a conical entry (angle = 15°) at a temperature of 190°C.

15 The measurement values clearly show that the moulding compound according to the invention in all cases resulted in better strength properties and also had better processing properties during production.

Table 2

For hollow articles testing, 500 ml round bottles were produced on a Bekum BAE 3 under the following conditions and with the following result:

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Example	1	2	3	4	CE 1
Base slot	150	150	150	150	200
Rotational speed [rpm]	17.7	17.7	17.7	17.7	--
Blowing time [sec]	15	14.0	12.0	11.2	12
Weight [g]	41.4	37.4	36.0	35.6	38
Wall thickness [mm]	1.2	1.00	0.90	0.85	--
Weld line thickness [mm]	2.0	2.0	1.0	1.0	(0.5) (V notch)
Melt fracture [score]	2	2	2	2	2
Fisheyes [score]	2	2	2	3	1
Note	matt	matt	matt	matt	matt

It can be seen that the moulding compound according to the comparative example forms an excessively thin weld line, which in addition has a V notch, which represents a weak point which may burst under pressure load.

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